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Immersion nanoimprint lithography using perfluoroalkyl liquid

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ABSTRACT

When an attempt is made to thermal-imprint on a thin film of thermoplastic coated on a hard-surface, e.g., an Si wafer, very often the amount of the fluidic resin is not found to be enough. In such cases any air trapped between the mold pattern, and the molding material is not sufficiently compressed by the imprint pressure, and which causes bubble defects. We then propose a novel technique where the air-space between mold pattern and the molding material is filled with a liquid material prior to the commencement of the heating and processing operations. Two characteristics required of the liquid material used for replacing the air are that the liquid does not evaporate at the imprint temperature, and that its liquidity improves with the rise in temperature. In our experiments, a mold heated up to 145 °C was pressed against a 460-nm thick polymethyl methacrylate (PMMA) film spin-coated on an Si wafer. To prevent the formation of bubble defects, we replaced the air with perfluorotributylamine with a boiling point of 174 °C. As the press operation progressed on, the perfluoroalkyl liquid from the inside of the mold pattern was pushed away to the outside, and the cavities of the mold pattern (from where the residual air was previously removed by the liquid) were filled with the soften PMMA. Thus an immersion nanoimprint technology that we propose here is expected to be one of the epoch-making solutions that can dramatically decrease the formation of defective moldings.

1. Introduction

Nanoimprint is a technology that can easily transfer nano-scale patterns in large quantities that involve a precise replication of patterns on a plastic material from a template fabricated by employing semiconductor manufacturing processes. Various technologies concerning nanoimprint have been developed and reported, and where various disciplines are involved in their applications [1]. Especially, a thermal nanoimprint has been employed as a production technique for optical devices and biochips, because there happen to be many choices for the molding material [2]. A bulk material of a thermoplastic was often processed and used as a substrate for devices. Also, a thin film of thermoplastic, spin-coated on an Si wafer, was imprinted for using the patterned thermoplastic film to serve as a masking layer in a dry-etching process [3]. As for the thermoplastic itself, its liquefaction rises remarkably when heated to above its glass transition temperature. Hence, a softened thermoplastic flows easily into the fine relief structures of the mold pattern when subjected to a press operation. The softened resin flows into the cavity of a concave mold pattern starting from the cavity's circumference, and then proceeds to trap the air into the cavity's center where under high imprint pressure the air is gradually compressed until the bubble defects disappear, and the cavity is completely filled with the thermoplastic [4]. A line of caution in this approach is that if the imprint pressure is terminated before the thermoplastic is sufficiently cooled down to some required temperature, the compressed air can expand and explode resulting in the formation of a fractal tree pattern generated radially and is known as "viscous fingering" [5]. Therefore, bubble defects easily occur in the mold pattern when the amount of the flowing molding material is insufficient [6]. For example, a thin film formed on an Si substrate provides insufficient flowing molding material because of its small thickness, that would not be encountered in case of bulk material [7]. When a mold pattern is not completely filled with the molding material, a defective molding is most likely to take place [8]. In order to prevent such defective moldings from occurring, techniques such as low pressure imprinting using a soft mold made by polydimethylsiloxane (PDMS) [9], vacuum imprinting under a decompressed environment [10], and ultrasonic nanoimprint assisting in the liquefaction of molding materials by ultrasonic vibration [11] have been reported. In this paper, we propose a novel technique that we name as "immersion nanoimprint" where a fluorine liquid is inserted between the mold pattern and the molding material. In conventional immersion lithography, high transfer accuracy is achieved by filling the space between a photoresist coated Si wafer and the imaging lens with pure water in order to extend the imaging capability of the lens in a photolithography system [12,13]. The contribution

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of the liquid material in our immersion technology, however, is different from the one in the conventional immersion lithography. Here a fluorine liquid is used to purge out the residual air that causes bubble defects.

2. Bubble defects in thermal nanoimprint

In the preparation for a molding substrate, a 2-in. Si wafer was spin-coated with polymethyl methacrylate (PMMA) in an ethylcellosolveacetate solution (OEBR-1000, Tokyo Ohka Kogyo) at a rotational speed of 4000 rpm. Next, it was run through a 20 min/170 °C bake that resulted in the formation of a 460-nm-thick PMMA layer on the substrate [14]. For this experiment, an Si mold NIM-80L RESO (NTT Advanced Technology), 10 mm^2 in size, with a pattern layout of 100 nm–3 μm linewidths, and 200 nm in depth was used. A fluorine release agent Optool HD-1101 (Daikin Industries) was spread on the patterned surface of the Si mold by dipping it into the solution [15]. A desktop thermal nanoimprint system NI-1075 (Nano Craft Technologies) [16] was used in the imprint experiment. The molding substrate was fixed on an upper ceramic heater of the nanoimprint system by a 2-mm thick Al sample holder as shown in Fig. 1. Then an Si mold bonded to a 3-mm thick glass-like carbon (GC) plate with a polyimide double-faced tape was fixed on a bottom ceramic heater. The Al sample holder and GC plate were pressed against the ceramic heaters by the help of hooks and springs. The Si mold and the PMMA coated Si wafer were heated up to 145 °C, which happened to be 40 °C higher than the glass transition temperature of PMMA (105 °C). The temperature on the surface of the Si mold and the PMMA thin film were adjusted by controlling the heating temperature of the upper and bottom ceramic heaters while monitoring those surfaces using a contacting surface thermometer. After the setup, the molding substrate was made to approach the mold at a speed of 1 μm/s by the servomotor drive; and after the contact was made the substrate was pressed against the mold for 10 s at an imprint pressure of 5 MPa. After the Si mold and the PMMA coated Si wafer were left to cool down to 95 °C, the molding substrate was then moved back to its initial position; that completed the processes. The imprint result under these conditions is shown in Fig. 2(a). Since the initial thickness of the PMMA film happens to be quite a bit larger than the height of the mold pattern, this figure shows the relief structure on the PMMA film's surface. Therefore, the variations in the color as seen through an optical microscope were caused by the interference of light resulting from the thickness distribution of the PMMA film. The left optical micrograph shows the pattern area around which a majority of defects existed, and is named as viscous fingering pattern in 30-μm wide convex space that existed around 3-μm wide concave line patterns caused by the explosion of a residual air. In the right optical micrograph, bubble defects were observed between the character patterns and a lower line pattern.

In the thermal nanoimprint, the conditions, namely imprint temperature, de-molding temperature, press force, press speed, and holding time have strong influence on the molding accuracy. In our experiments, the imprint temperature and the de-molding temperature were fixed to 145 and 95 °C, respectively, while other conditions were made to vary, and the appearance of viscous fingering patterns was recognized and recorded. Fig. 2(b and d) shows the experimental results in the case of increasing the press force up to 1000 N, extending the holding time to 60 s, and decreasing the press speed to 0.1 μm/s. However, it became quite clear that none of the conditions were satisfactory in preventing the formation of bubble defects that gave rise to the defective molding.

3. Effect of immersion by fluorinert

In common practice, a perfluoroalkyl liquid is used to form a self-assembled monolayer (SAM) on the mold surface, by dipping the mold into the liquid. The purpose there is to minimize the release force in the de-molding process associated with thermal nanoimprint [15,17]. However, in our immersion technique, a perfluoroalkyl liquid was used for a different purpose. Here Fluorinert FC-43 (3M) [18], a chemically stable liquid at the imprint temperature (Table 1), was used as perfluorotributylamine that was inserted between the Si mold and the PMMA thin film. In actual experiment, after the mold and the molding substrate were set up, Fluorinert FC-43 was dispensed on the surface of the mold pat-

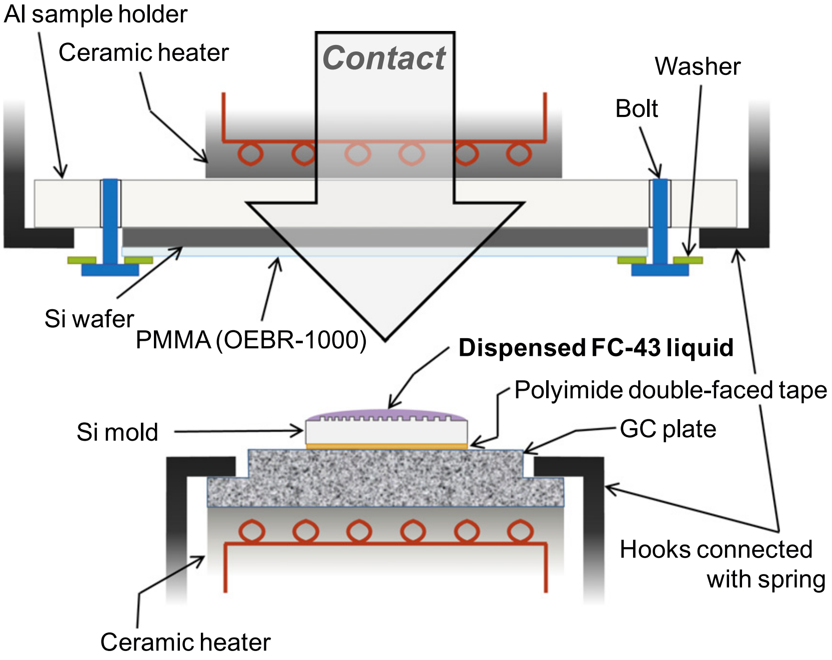

Fig. 1. Setup of mold and molding material after a perfluoroalkyl liquid was dispensed on the mold patterns.